levels

$$\epsilon=\epsilon_1-(n+\tfrac{1}{2}),$$

$$\epsilon_1=\tfrac{1}{2}\mathcal{E}_g\left\{\left[1+\frac{4[\epsilon_0+(n+\frac{1}{2})+\epsilon_3+\epsilon_4]}{\mathcal{E}_g}\right]^{\frac{1}{2}}-1\right\}. \qquad \text{(B-17)}$$

Here the $n+\frac{1}{2}$ appears from using $\mathcal{E}'$ in Eq. (B-5), and ϵ_0 is given by Eq. (B-13) with d redefined:

$$d=\Delta(1+\epsilon_1/\mathcal{E}_g)+r_2-\epsilon_0. \qquad \text{(B-18)}$$

For ϵ_3, if the valence band effective mass Hamiltonian is $\mathcal{H}(F,G,H_1)$, using the parameters of Eq. (B-6), then

$$\epsilon_3=(\epsilon_1/\mathcal{E}_g)(\langle\mathcal{H}(0,G,H_1)\rangle+n+\tfrac{1}{2}), \qquad \text{(B-19)}$$

where we can take the expectation value with respect to the wave functions in Eqs. (22) and (27) since this is a small correction.

Finally ϵ_4 is the contribution of D_1 in reference 4, and is obtained from second order perturbation theory, using Eqs. (22) and (27), since again this is a small correction.

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Optical Properties of Nickel and Tungsten and Their Interpretation According to Drude's Formula

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New optical data are reported for nickel at 88°, 298°, and 473°K and for tungsten at 298°, 1100°, and 1600°K in the wavelength range 0.365 to 2.65 microns. These data are shown to depend on wavelength in a way which is in good quantitative agreement with a formula initially proposed by Drude. By attributing different terms in Drude's equation to the motion of different classes of free and bound electrons, one may conclude that several classes of each are present in both metals. Each class of free electrons accounts for a portion of the dc conductivity and has its own characteristic relaxation time or wavelength. From this analysis it appears that most of the dc conductivity may be attributed to one class of free electrons, although optical properties are strongly influenced by other classes as well. In both metals the characteristic wavelength λ_{r1} of the first class of free electrons proves to be proportional to the corresponding conductivity σ_1 at different temperatures. In nickel the constant ratio σ_1/λ_{r1} accounts for the low temperature coefficient of optical properties throughout the visible and near infrared range. In tungsten this constant ratio contributes to the existence of the x-point or cross-over wavelength in the spectral emissivity. It is shown that the anomalous skin effect may not be a significant factor in the measured optical properties of a metal like nickel in the range of wavelength where these properties have only a small temperature coefficient.

I. HISTORICAL ORIENTATION

OPTICAL properties of thick metal specimens may be measured most readily by reflected light. The principles for doing this were worked out many years ago and were carried to a high state of refinement by Drude.[1] Drude[2] also showed that the observed optical properties depended on wavelength in a rational manner. On the basis of this analysis he claimed that there were at least two kinds of charged particles which could move freely in the metals he studied. He called them "ions" but was unable to give a satisfactory theory to account for them. Nevertheless, Drude[3] did point out that other properties such as Hall effect and thermoelectric phenomena likewise indicated the presence of two kinds of charge carriers. Drude's "ion hypothesis," however, was not well received by his contemporaries. In a recent paper (hereafter referred to as paper I) the author[4] appears to have been the first since Drude to recommend that serious consideration be given to this interpretation of optical properties of metals.

In paper I and in the present work the author reports that the interpretation depending on the implied existence of more than one class of free electrons, distinguished by their different relaxation times, is highly successful in describing the optical properties *versus* wavelength of a variety of metals. One might wonder, perhaps, why such a simple fact has remained so long in obscurity. It may be that an appropriate reason is suggested in these words of Lucretius: ". . . no fact is so simple that it is not harder to believe than to doubt at the first presentation." The circumstances related below certainly indicate that the above fact was very difficult to believe in Drude's time.

Schuster[5] appears to have been the first to have suggested that, since electrons in a metal were the same as those observed in cathode rays, they should all have the same charge, the same mass, and in each metal a single relaxation time. In the absence of quantum mechanics this argument seemed quite logical. In

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[1] P. Drude, Ann. Physik **39**, 481 (1890).

[2] P. Drude, Physik. Z. **1**, 161 (1900).

[3] P. Drude, Ann. Physik **1**, 566 (1900); **3**, 369 (1900); **7**, 687 (1902).

[4] S. Roberts, Phys. Rev. **100**, 1667 (1955).

[5] A. Schuster, Phil. Mag. **7**, 151 (1904).

response to this criticism Drude[6] tentatively modified his interpretation by dropping from consideration all but one kind of free electrons. Lorentz[7] also thought there were compelling reasons for admitting the existence of only one kind of free electrons in metals, even though this was admittedly in contradiction to observations of the Hall effect.

It is the resulting simplified version of Drude's treatment, with only a single "universal" relaxation time for free electrons, which has been transmitted to us by subsequent writers including Sommerfeld and Bethe,[8] Zener,[9] Mott and Zener,[10] Mott and Jones,[11] Wilson,[12] Kronig,[13] Seitz[14] and so forth. The same version has been used more recently by Beattie and Conn[15] and by Schulz.[16] Nevertheless, it does not appear to the author that the optical properties of metals have ever been accounted for satisfactorily on the basis of only one type of free electrons. In tacit recognition of this fact Wilson,[12] in the second edition of "The Theory of Metals," reluctantly omitted the entire section on optical properties which had appeared in the first edition.

The arguments in favor of the limitation to a single type of free electrons advanced by Lorentz and others have lost their force with the development of the energy band model for the behavior of different classes of electrons in solids. Furthermore, since Drude's time there has been a substantial accumulation of additional nonoptical evidence[17] to support the conclusion that in various metals at least two distinct classes of electrons take part in the electrical conductivity. In view of the wide acclaim accorded to Drude's revised (1904) interpretation of optical properties, it does seem significant to point out even now that his original interpretation is in better agreement with both optical and nonoptical experimental evidence. Evidently Drude[18] thought so too, for in the second edition of his *Lehrbuch der Optik*, completed in manuscript form just prior to his death, he once again put forward the proposition that more than one type of free electrons ought to be considered when accounting for the optical properties of metals [i.e., in Eqs. (41) and (44) on p. 386].

In the ensuing years the electronic theory of metals has undergone many changes, but the experimental facts known to Drude have mostly remained the same. Additional optical data only reinforce Drude's original interpretation. The details of metallic reflection do not appear to be understandable by any other approach. The theoretical climate now seems more favorable, as pointed out in paper I. In the present work the author offers further data which not only confirm Drude's initial interpretation but which also lead to new conclusions in extension of it.

II. FUNDAMENTAL CONSIDERATIONS

The laws of refraction and reflection of polarized light by a plane interface between two isotropic homogeneous media were originally worked out by Fresnel. These laws, when written with complex coefficients, apply to absorbing media as well as to transparent ones. They express the amplitude and phase of the refracted wave and the reflected wave relative to the incident wave for arbitrary angle of incidence depending on the nature of the two media. In the present instance, one of the media is to be vacuum and the second is to be a metal. The wave refracted into the metal is lost by absorption in a thick specimen, so that only the incident and reflected waves are accessible for control and measurement.

If the incident wave is polarized at arbitrary azimuth, it may be resolved into two components with electric fields, respectively, parallel and perpendicular to the plane of incidence. Each of these components suffers a definite reduction in amplitude and a shift in phase upon reflection from an isotropic medium. A single complex reflection coefficient describes both changes in either component, but the two components of the wave have different reflection coefficients. Hence their ratio is a complex number different from unity. Drude[19] showed how to measure this ratio, namely that of the reflection coefficient for light polarized parallel to the plane of incidence to that for light polarized at right angles to this. He expressed this ratio in the form $\tan\psi e^{i\Delta}$. His notation is retained here, as is also his convention for the direction of positive vectors in the incident and reflected waves.

Fresnel's equations for reflection of light at a plane interface between two homogeneous isotropic media

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[6] P. Drude, Ann. Physik **14**, 936 (1904).

[7] H. A. Lorentz, Koninkl. Akad. Wetenschap. Amsterdam **7**, 438, 585 and 684 (1905).

[8] A. Sommerfeld and H. Bethe, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), second edition, Vol. 24, Part 2, p. 579.

[9] C. Zener, Nature **132**, 968 (1933).

[10] N. F. Mott and C. Zener, Proc. Cambridge Phil. Soc. **30**, 249 (1934).

[11] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, Oxford, 1936), p. 110.

[12] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1936 and 1953), first edition, p. 124; second edition, preface.

[13] R. DeL. Kronig, Proc. Roy. Soc. (London) **A133**, 255 (1931).

[14] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940) p. 638.

[15] J. R. Beattie and G. K. T. Conn, Phil. Mag. **46**, 989 (1955).

[16] L. G. Schulz, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1957), Vol. 6, p. 102.

[17] N. F. Mott, Proc. Phys. Soc. (London) **47**, 571 (1935); Proc. Roy. Soc. (London) **A153**, 699 (1936); **A156**, 368 (1936); H. Jones, Proc. Roy. Soc. (London) **A155**, 653 (1936); A. H. Wilson, Proc. Roy. Soc. (London) **A167**, 580 (1938); E. H. Sondheimer and A. H. Wilson, Proc. Roy. Soc. (London) **A190**, 435 (1947); E. H. Sondheimer, Proc. Roy. Soc. (London) **A193**, 484 (1948); M. Kohler, Ann. Physik **5**, 89, 99, 181 (1949); **6**, 18 (1949); R. G. Chambers, Proc. Phys. Soc. (London) **A65**, 903 (1952); B. R. Coles and J. C. Taylor, J. Phys. Chem. Solids **1**, 270 (1957); E. J. Moore, Australian J. Phys. **2**, 235 (1958).

[18] P. Drude, *Lehrbuch der Optik* (S. Hirzel, Leipzig, 1906), second edition.

[19] P. Drude, *The Theory of Optics* (Longmans, Green and Company, New York, 1902) p. 361.

may be written as follows:

$$R_s = \sin(\phi_2 - \phi_1)/\sin(\phi_2 + \phi_1),$$
$$R_p = -\tan(\phi_2 - \phi_1)/\tan(\phi_2 + \phi_1). \qquad (1)$$

In the above equations R_s is the complex reflection ratio for light having its electric vector perpendicular to the plane of incidence and R_p is the reflection ratio for light polarized parallel to that plane. ϕ_1 is the angle of incidence in the vacuum and ϕ_2 is the angle of the refracted wave in the metal. In an absorbing medium, such as a metal, the latter angle is a complex number as evidenced by the fact that planes of constant phase do not coincide with planes of constant amplitude.

The following ratio is measured according to Drude's procedure:

$$R_{sp} = R_p/R_s = -\cos(\phi_2 + \phi_1)/\cos(\phi_2 - \phi_1) = \tan\psi e^{i\Delta}. \quad (2)$$

The square of the complex index of refraction of the metal, or its "dielectric constant" K, is related to the angles ϕ_1 and ϕ_2 by Snell's law:

$$K = \sin^2\phi_1/\sin^2\phi_2. \qquad (3)$$

By elimination of ϕ_2 in Eqs. (2) and (3) one obtains the following result for K which should be a fundamental property, specifically independent of the angle of incidence, ϕ_1:

$$K = \sin^2\phi_1\left[1 + \tan^2\phi_1\left(\frac{\cot 2\psi - i\sin\Delta}{\csc 2\psi + \cos\Delta}\right)^2\right]. \qquad (4)$$

The dielectric constant K is to be resolved into real and imaginary parts in the following way:

$$K = K' - iK''.$$

The propagation of electromagnetic waves in a homogeneous isotropic medium is described according to Maxwell by a set of equations involving only two parameters which characterize the medium at a given wavelength. These are the dielectric constant K and the magnetic permeability μ. In deriving Eq. (4) it was assumed that the permeability of the metal is that of free space. This is generally thought to be a good approximation even in ferromagnetic metals such as nickel at the wavelengths under consideration. Fresnel's equations themselves are a consequence of Maxwell's hypothesis concerning the electromagnetic nature of light.

If the surface of the metal is nonhomogeneous, if it is anisotropic, if its magnetic permeability is different from that of vacuum, or if there is any other factor that would bring about a significant deviation from the assumptions on which Eq. (4) is based; then it follows that the value of K as defined by Eq. (4) may not necessarily be independent of ϕ_1. Conversely, if measurements of ψ and Δ at different angles of incidence yield different values of K according to Eq. (4), then one may question the validity of Fresnel's or Maxwell's equations for the surface being measured. Drude[1] studied this matter very carefully and he did observe deviations from Eq. (4) which he attributed to surface films and to fine scratches. Drude[20] also derived equations for reflection from surfaces covered with thin films. From these equations it may be inferred that such surfaces would not be expected to have any fixed value of K at different angles of incidence, if K is defined by Eq. (4). A nonconstant value is actually observed for surfaces covered by films such as those produced by moisture, grease, oxide layers, etc. Drude noticed that the surface films which appeared on his specimens were of nonuniform thickness, a fact which resulted in nonuniform polarization in the light reflected from different parts of the specimen. By paying special attention to the preparation of the surface he was successful in eliminating these extraneous effects and in obtaining values of $\sqrt{K}$ which were independent of the angle of incidence and which were truly representative of the metal being studied. The square root of K is called the "complex index of refraction" and is generally written in one of the forms: $n(1-i\kappa)$ or $n-ik$.

Having defined K in the above manner and having measured it at different wavelengths, one is naturally led to inquire whether there is some simple formula which expresses the observed relationships in a concise manner. The following formula, adapted from Drude's expression[19] [Eq. (39), p. 398] has proved entirely adequate for this purpose:

$$K = 1 + \sum_m \frac{K_{0m}\lambda^2}{\lambda^2 - \lambda_{sm}^2 + i\delta_m\lambda_{sm}\lambda} - \frac{\lambda^2}{2\pi c\epsilon_0}\sum_n \frac{\sigma_n}{\lambda_{rn} - i\lambda}, \qquad (5)$$

where λ is the wavelength in vacuum, c is the velocity of light, and ϵ_0 is the permittivity of vacuum (in mks units). The other parameters appearing in Eq. (5) are arbitrary coefficients which are adjusted independently to characterize any given metal.

If one considers λ to be a complex variable, then Eq. (5) just states that K is given by an analytic function of λ having only simple poles, including the pole at infinity. This equation is not quite the most general such function that one might conceive consistent with considerations of "physical realizability" as are employed, for example, in discussing driving point impedance functions of electrical networks; but it seems to be sufficiently general to be adaptable to existing experimental data for optical properties of metals. Similar functions have been obtained in specific instances either by classical or by quantum mechanical theories. The really important common element in both of these treatments seems to be that the time dependence is introduced in the form of a linear differential operator. Equation (5) might apply just as well for any of a broad class of theories in which the time dependence is treated by the methods of linear operational calculus.

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[20] P. Drude, Ann. Physik **36**, 865 (1889).

On this basis Eq. (5) is not to be identified solely with some particular atomic theory, but instead it should be regarded as a mathematical hypothesis which stands by itself.

One might hope that a finite number of terms in Eq. (5) would be sufficient in any given metal for complete accord with experiment. In this case the equation would also be a unique representation of the dielectric constant *versus* wavelength. If there is a unique relation, one may confidently expect any valid atomic theory to lead to it. It has been found that the above hope is fulfilled, and in consequence of these remarks it follows that, while Eq. (5) may not be a theory in itself, its application unquestionably may provide guidance in testing the relative appropriateness of different theories. It is fitting and proper that experimental results should be considered in this way in the eventual formulation of a theory.

If one evaluates the parameters in Eq. (5) by fitting curves to experimental data, one might expect to find a clue concerning the natural laws which govern the values of these parameters. This was Drude's approach, which led him into contradiction with the best theories of his day. His method remains valid today, but the contradiction with theory no longer exists, as noted initially in paper I. The author has now carried this method a step further and has shown that certain parameters in Eq. (5) are interrelated in a manner which was not known by Drude or others until now.

The effective conductivity σ at a wavelength λ may be defined by the relation

$$\sigma = 2\pi c\epsilon_0 K''/\lambda, \tag{6}$$

where K'' is the negative imaginary part of K. If Eq. (5) is extrapolated to very low frequencies, or long wavelengths, one obtains the limiting value:

$$\sigma_0 = \sum_n \sigma_n. \tag{7}$$

This, then, is the dc conductivity. In Eq. (5) each component σ_n of the dc conductivity is characterized by a specific relaxation wavelength λ_{rn}. In the past it has been customary to attribute seeming inconsistencies between optical properties and dc conductivity to some surface condition of the metal. In the author's interpretation no such inconsistency has arisen, for it has always been possible to choose a single set of parameters which gives good results both in Eq. (5) and in Eq. (7).

In discussing Eq. (5) and in applying it, it is necessary to have names for the specific terms of which it is made up. The names which will be used carry the implication that all terms except unity are a result of the motion of electrons, and conversely that the motion of each electron contributes to one or another term in Eq. (5) at any given moment. Since the terms containing σ_n and λ_{rn} all contribute to the dc conductivity, they may be attributed to the same electrons which give rise to the conductivity; i.e., "conduction" electrons or "free" electrons. Likewise, since the other terms, those containing K_{0m}, contribute nothing to the dc conductivity, they may be attributed to unfree or "bound" electrons. In the following discussion the expressions "free electrons" and "bound electrons" are meant to be names referring to specific terms in Eq. (5) and are not intended to have any deeper theoretical significance except where definite theories are mentioned.

Stated in the above language, the principal conclusion of paper I was that the optical properties of a number of metals were consistent with Eq. (5), but that generally at least two free-electron terms were indicated, thereby implying the existence of two classes of conduction electrons. In the present paper a study of the temperature dependence of optical properties confirms the above result and in addition shows that there is one class of free electrons, accounting for most of the dc conductivity, for which the ratio σ_1/λ_{r1} is independent of temperature. This relation holds over wide variations of σ_1 and λ_{r1} and plays a part in two seemingly diverse phenomena which have heretofore seemed rather puzzling. One of these is the fact[1] that the optical properties of certain metals in a range of wavelength have much smaller temperature coefficients than one would ordinarily expect if the dc conductivity had any direct bearing on the optical properties. The other effect is the crossover or x-point[21] observed in the spectral emissivity of a number of refractory metals and metallic compounds. This is a single wavelength at which there is virtually no change in emissivity even over a wide range of temperature. At shorter wavelengths the emissivity has a negative temperature coefficient and at longer wavelengths a positive one. Both the generally low temperature coefficient and the existence of a crossover point, observed in different metals, are here shown to be associated with the constancy of the ratio σ_1/λ_{r1}.

Now that the constancy of the ratio σ_1/λ_{r1} is recognized, it seems natural that this ratio should be constant. In Drude's[19] theory, the ratio σ_1/λ_{r1} is proportional to N_1e^2/m_1, where N_1 is the concentration of the primary class of free electrons, e is the electronic charge, and m_1 is the corresponding effective mass. When Drude[6] revised his treatment so as to exclude all but one type of free electrons, he had to postulate that the parameters corresponding to σ and λ_r were functions of wavelength. To explain the small observed temperature coefficient of optical properties he was led to assume, in effect, that both σ and λ_r in the wavelength range of visible light were insensitive to temperature. This is quite different from the author's interpretation according to which both σ_1 and λ_{r1} depend a great deal on temperature, but not on wavelength, and just maintain a constant ratio as the temperature changes. In Drude's revised interpretation Ne^2/m, as determined experimentally, depends to a certain extent on wave-

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[21] D. J. Price, Proc. Phys. Soc. (London) **59**, 131 (1947).

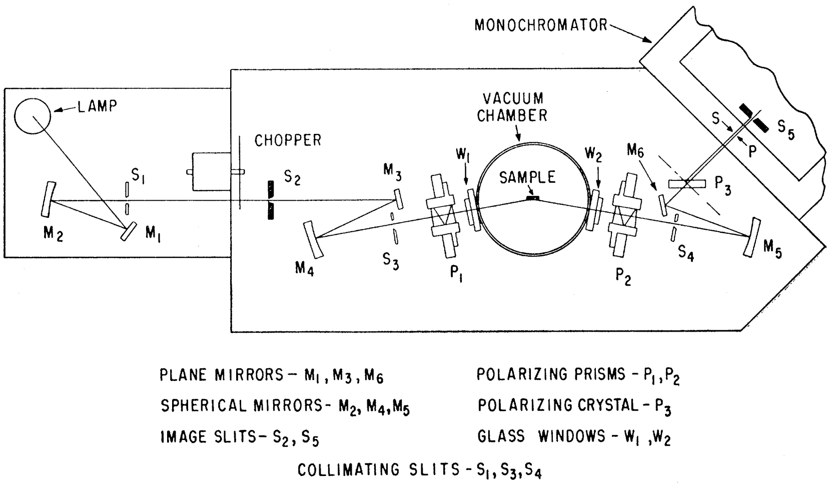

FIG. 1. Plan of optical system.

length and is both numerically and conceptually different from the corresponding ratio N_1e^2/m_1 when two classes of free electrons are thought to be present.

Sondheimer,[22] in reviewing work on electronic mean free paths, pointed out the constancy of the ratio of the conductivity to the mean free path. If two classes of free electrons are present and if one class accounts for most of the dc conductivity, it seems almost a trivial step to infer from mean free path data that σ_1/λ_{r1} should be independent of temperature; and yet it is a step that does not appear to have been taken until now. Certainly it has never been appreciated that the constancy of this ratio exerts a powerful influence on the optical properties of metals and that it therefore can be demonstrated by experiment.

The experimental work upon which these conclusions are based consists of a study of the optical properties of two metals, each over a wide range of temperature and wavelength. Nickel is an example of a metal with optical properties having a low temperature coefficient. Tungsten is an example of a metal having a crossover or x-point in its emissivity. Tungsten turned out to be a rather complex metal to analyze by Drude's method, yet after much labor both metals were found to be fully consistent with Eqs. (5) and (7) within limits which are thought to be attributable to experimental error.

III. EXPERIMENTAL PROCEDURE

In his experiments Drude used incident light polarized at an azimuth of 45° and he analyzed the reflected light by means of a Soleil-Babinet compensator in conjunction with a Nicol prism. In extending the wavelength range for observations in the infrared it has been found desirable to dispense with the compensator and to rely instead on photometric methods of measurement. The systematic procedure for doing this was worked out in recent years independently by Beattie[23] and by Hodgson.[24] The method employed by the author involves a slight modification of their techniques in that a third polarizing element is employed just in front of the monochromator. The third polarizing element insures that the measurements will be independent of the relative sensitivity of the monochromator to light polarized in different directions in addition to being independent of the state of polarization of the light source.

The plan of the optical system is shown in Fig. 1. The light source is a tungsten lamp with a ribbon filament 2 mm wide. This was supplemented at shorter wavelengths by a mercury arc in order to obtain increased intensity. The light is reflected from a plane diagonal mirror M_1 and a spherical mirror M_2 which focuses an image of the filament on the slit S_2, which has an opening 1 mm wide. The slit S_1 restricts the horizontal angular width of the beam to 2°. A rotating chopper is located in front of the slit S_2. An image of the slit S_2 is brought in focus on the sample at the fixed angle of incidence, 80°, by means of the plane mirror M_3 and the spherical mirror M_4. The slit S_3 again limits the horizontal angular width of the beam to 2°.

The metal sample is mounted inside a metal vacuum chamber fitted with thick light-flint glass windows to pass the incident and reflected beams. The windows are not clamped in place, but are held by the air pressure against O-ring seals. In this way uneven strains are avoided and the windows do not alter the polarization of the light passing through them within the accuracy of the measurements.

The main polarizing prisms, P_1 and P_2, are mounted in rotators with scales readable to 0.1° and are located just outside the two windows in the path of the incident and reflected beams, respectively. These prisms are a modification of the prism attributed to Abbé by

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[22] E. H. Sondheimer, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1952), Vol. 1, p. 1.

[23] J. R. Beattie, Phil. Mag. **46**, 235 (1955).

[24] J. N. Hodgson, Proc. Phys. Soc. (London) **B68**, 593 (1955).

Thompson.[25] In this design a short prism of large aperture could be made with a uniform field of polarization and many of the other desirable features of the longer and more costly Glan-Thompson prism. The wide range of wavelength in which this prism may be used results from a fortuitous match of the indices of refraction of fluorite and of the *E*-ray of calcite.

The beam reflected from the sample is brought to focus on the entrance slit S_5 of the monochromator by means of the spherical mirror M_5 and the plane mirror M_6. This would ordinarily form a single image of the sample at this point; however, a cleavage plate of calcite P_3 is mounted as shown and this splits the beam so as to form two images of the sample. As indicated, the calcite crystal is inclined at an angle so that its optic axis is nearly perpendicular to the light path. One image consists of radiation polarized perpendicular to the horizontal plane, while the other image consists of radiation polarized parallel to that plane. Only a slight rotation of the calcite crystal is needed to bring either image into coincidence with the slit S_5.

The monochromator is a standard Littrow-type instrument using a light-flint glass prism. The transmitted monochromatic radiation is focused by an ellipsoidal mirror onto a small lead sulfide photoconductive cell. The ac component of the photocurrent from the lead sulfide cell is amplified and converted to to a dc signal by a synchronous rectifying contact on the light chopper. The experimental method of determining ψ and Δ, using the apparatus described above, will be described elsewhere.

Two different methods are used for mounting the samples in these experiments. The experiments on nickel are done on a bar of dimensions 8×5×50 mm. This is mounted inside a small copper box which is attached to a flange on the bottom of a well which is built into the center of the flat top plate of the vacuum chamber. The copper box has openings to transmit the incident and reflected radiation and it may be heated by an electric heater placed at the bottom of the well. Alternatively the box containing the sample may be cooled by pouring liquid nitrogen into the well. To prevent condensation on the surface of the sample, the openings in the copper box are covered by glass windows.

The tungsten sample is in the form of a ribbon of dimensions 0.12×8×50 mm. This is clamped at each end in such a way that it can be heated by an electric current. The well, mentioned above, is used as an additional cold trap so that a good vacuum is maintained in all the measurements on tungsten. The rest of the vacuum system is of conventional design and therefore requires no special description.

IV. OPTICAL CONSTANTS OF NICKEL

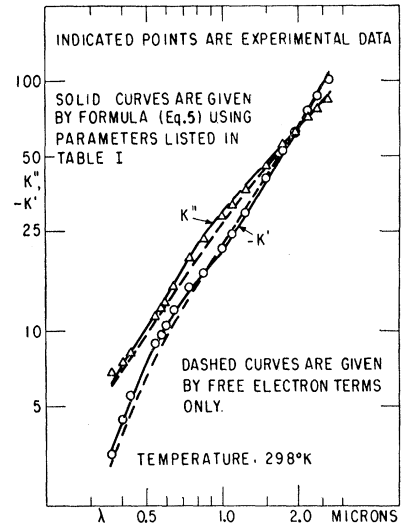

FIG. 2. Observed optical constants of nickel at 298°K.

The nickel used in the experiments described here was prepared from nickel carbonyl and was vacuum-melted. This process normally produces material of about 99.98% purity, the principal impurity being carbon. The bar was machined to shape and was ground flat on one side. After being annealed in hydrogen at 950°C, the bar was electropolished in a solution made according to the following recipe.

H_3PO_4 (85%) : 453.6 g;
$Al_2(SO_4)_3 \cdot 18H_2O$: 188.6 g;
$NiSO_4 \cdot 6H_2O$: 14.25 g.

The temperature of the electropolishing bath was 80°C and the current density was about 40 amperes/(decimeter)^2. The cell was operated for 5 minutes at 6 volts. This treatment smoothed the surface, removed the tool marks and left a bright mirror finish which was sufficiently flat so that the reflected beam in the optical system retained the desired degree of collimation. On microscopic examination it appeared that different crystal grains were dissolved to slightly different levels. The surfaces of individual grains appeared very smooth and free of light-scattering defects.

Measurements on nickel at room temperature, 298°K, gave the results indicated in Fig. 2. These data are mostly in accord with older results analyzed in paper I. However, the present analysis of the data is different in several minor respects. This time, with what are believed to be more accurate data, there seems to be definite evidence of a bound-electron term with its characteristic wavelength λ_{s1} at 0.85 μ. This and the other parameters obtained by fitting curves to the experimental data at 298°K are shown in the second column of figures in Table I. It should be observed that a different scheme of notation is used here from that employed in paper I. If one omits the bound electron term involving K_{01}, while retaining K_{02}, one obtains the dashed curves in Fig. 2. From the compari-

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[25] S. P. Thompson, Proc. Optical Conv., London, p. 216 (1905).

TABLE I. Results of analysis of optical data for nickel.[a]

Temp.	88°K	298°K	473°K
σ_1	136.2	13.64	5.77
σ_2	0.365	0.365	0.365
σ_3	0.195	0.195	0.195
λ_{r1}	587.1	58.8	24.9
λ_{r2}	0.70	0.70	0.70
λ_{r3}	<0.36	<0.36	<0.36
K_{01}	1.05	2.1	2.85
K_{02}	1.2	1.2	1.2
λ_{s1}	0.85	0.85	0.85
λ_{s2}	<0.36	<0.36	<0.36
δ_1	0.35	0.70	0.95
σ_1/λ_{r1}	0.232	0.232	0.232
σ_0	136.8	14.20	6.33

[a] Conductivities (σ_1, etc.) are in units of 10^6 ohm^{-1}m^{-1}. The dc conductivity is σ_0. Wavelengths (λ_{r1}, λ_{s1}, etc.) are in microns.

son between these and the solid curves it is evident that the bound electron term actually amounts to only a small perturbation on otherwise smooth curves for K' and K'' *versus* wavelength.

Values of relative conductivity of 99.97% Ni at different temperatures as reported by Potter[26] and the absolute conductivity of 99.99% Ni at 0°C as reported by the National Bureau of Standards[27] were used in determining values of σ_0 in Table I. The procedure of adjusting parameters in the formula so as to fit the experimental data made it possible to determine σ_2, σ_3, and σ_1/λ_{r1}. For reasons to be explained later neither σ_1 nor λ_{r1} could be determined directly. Hence σ_1 was chosen so as to satisfy Eq. (7) and λ_{r1} was then determined from the known ratio σ_1/λ_{r1}.

It may be significant to compare the observed values of K' and K'' with values that are calculated for a single free-electron term. Figure 3 shows curves for K''/λ and $(K'-1)/\lambda$ which correspond to the same data represented by the smooth curves in Fig. 2. These may be compared with the curves for K_{r1}'/λ and K_{r1}''/λ, which are calculated for the single free-electron term which dominates the dc conductivity. The real part, K_{r1}'/λ accounts for a major part of $(K'-1)/\lambda$, especially at longer wavelengths, but K_{r1}'' is orders of magnitude too small. K_{r1}''/λ also shows the wrong dependence on wavelength, since it increases in the order of 50 times as λ goes from 0.365 to 2.65 micron, while the observed value of K''/λ only doubles. It is thus clear that the observed results cannot possibly be explained by a single free-electron term.

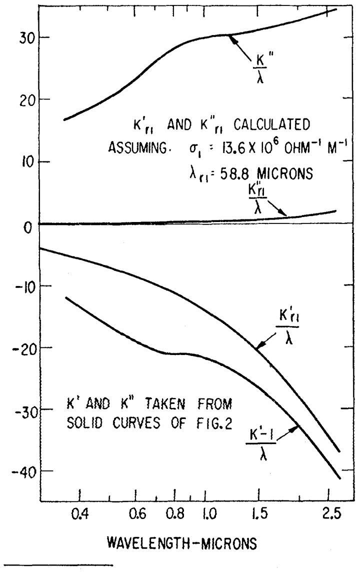

FIG. 3. Optical constants of nickel at 298°K compared with single free-electron term.

The optical constants of the nickel bar were likewise measured at 88°K and 473°K. In similar fashion these data were used in the determination of sets of parameters shown in the first and third columns of Table I. In each case the adjustment of parameters resulted in curves which fit the experimental data as well as the room temperature curves shown in Fig. 2.

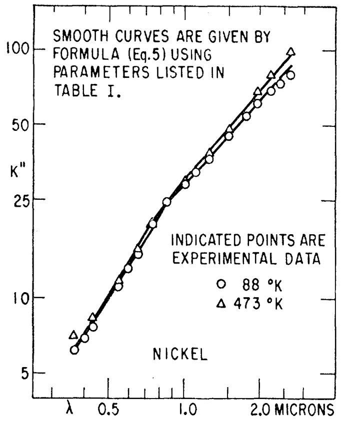

FIG. 4. Imaginary part of dielectric constant of nickel at 88°K and 473°K.

In fact very little difference in optical constants could be observed at these extreme temperatures despite a 20:1 change in dc conductivity. There was no observable change in K' that could be attributed to the free-electron terms; however, the perturbation due to the bound-electron term was more clearly resolved in the low-temperature curve for K', thereby indicating a smaller value of δ_1. A somewhat greater change in K'' could be observed and this is shown in Fig. 4.

The validity of the analysis of nickel is upheld by its extrapolation to longer wavelengths. The optical constants calculated in this way are shown in Fig. 5 in a range which extends to five times the longest wavelength used in the measurements. The calculated curve agrees with the experimental results of Beattie and Conn[15] to within the differences they observed in different specimens. Older data[28] are shown in Fig. 5 for comparison at the shorter wavelengths.

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[26] H. H. Potter, Proc. Phys. Soc. (London) **49**, 671 (1937).

[27] Natl. Bur. Standards Circ. No. 485 (1950).

[28] G. Quincke, Poggend. Ann. Jubelband 336 (1874); L. R. Ingersoll, Astrophys. J. **32**, 282 (1910); A. Q. Tool, Phys. Rev. **31**, 1 (1910).

Not only are the extrapolated values of K' and K'' in close agreement with the experimental data of Beattie and Conn; but the calculated temperature coefficients of these properties are likewise in close agreement. At a wavelength of 11 microns Beattie and Conn observed K'' to increase in a ratio 1:1.4 when the temperature was raised from 293°K to 533°K. In this same interval the conductivity decreases in a ratio 3.1:1. In the present interpretation it is perfectly clear why the value of K'' should not change in the same ratio as the conductivity. At 2 microns it hardly changes at all, but at 12 microns, according to the above interpretation, it should change in a ratio 1:1.49 when the temperature is raised from 298°K to 473°K. In this interval the dc conductivity decreases by a ratio 2.24:1. According to this interpretation the changes in optical constants *versus* temperature observed by Beattie and Conn are in reasonably good agreement with the changes in dc conductivity.

V. OPTICAL CONSTANTS OF TUNGSTEN

Tungsten ribbons were cut to a size 8×50 mm from a flat rolled sheet 0.125 mm thick and with the direction of rolling, respectively, parallel and perpendicular to the long dimension of different specimens. The direction of rolling made no difference in the results to be described. The sheet consisted of pure undoped tungsten supplied by the Lamp Wire and Phosphors Department and claimed to be of 99.99% purity. The ribbon to be measured was initially mounted in the evacuated measuring apparatus for a preliminary heat treatment. The heating current was increased slowly until the midpoint of the ribbon reached 2000°K. Then it was heated more rapidly to 2500°K. This treatment recrystallized the tungsten sufficiently so that its appearance and optical properties did not change significantly during subsequent measurements.

The tungsten ribbon was removed from the vacuum system after the above heat treatment and was electropolished at 25°C in a solution containing 30 g of NaOH per liter. The operating potential difference was seven volts, and the anode current density was 20 amp/dm^2. A stainless steel cathode was used.

The electropolished tungsten was bright and shiny and the beam reflected from it retained a satisfactory degree of collimation, although of course the surface was far from being optically flat. A small amount of scattered light could be observed under oblique illumination and this was traceable to the fine network of grain boundaries. It is believed that the observed scattered light should have no effect on the intensity ratio measurements. The surface of individual grains appeared free of light-scattering defects.

The results shown in Fig. 6 were obtained on the electropolished ribbon at room temperature. The data for K'' show two maxima which were also characteristic of all preliminary work on various tungsten samples, including a thick bar which was not heat treated.

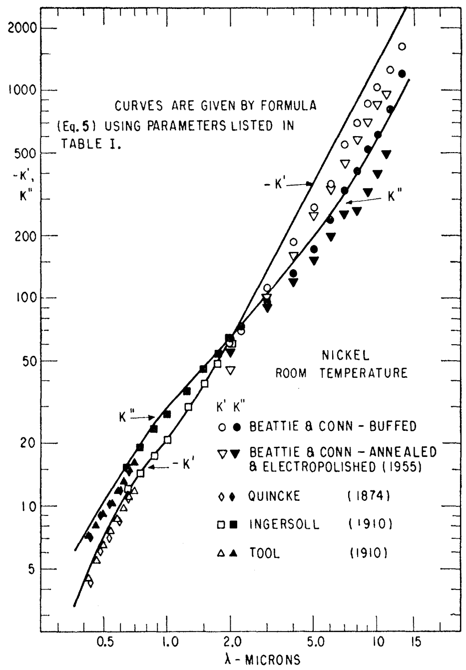

Fig. 5. Reported optical constants of nickel *versus* calculated curves.

Likewise the unpublished work of Barnes[29] showed a few scattered points which, though insufficient by themselves to determine a smooth curve at room temperature, are consistent with the same maxima. The slight rise at short wavelengths makes it seem likely that more measurements in the ultraviolet might reveal another maximum there.

It is only the bound-electron terms in Eq. (5) that can account for maxima in K''. Hence it is evident that at least three bound-electron terms are needed in the formulation of K for tungsten. The complete analysis of the data for tungsten at room temperature

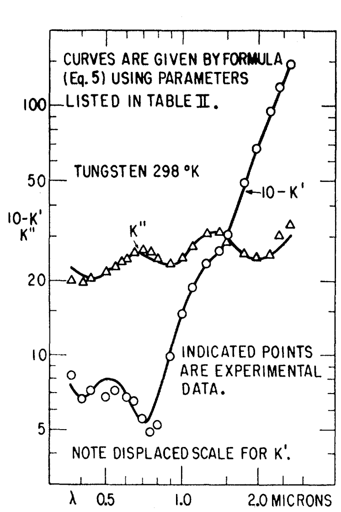

Fig. 6. Observed optical constants of tungsten at 298°K.

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[29] B. T. Barnes (private communication).

TABLE II. Results of analysis of optical data for tungsten.[a,b]

Temp.	298°K	1100°K	1600°K	2000°K	2400°K
σ_1	17.50	3.50	2.14	(1.58)	(1.19)
σ_2	(0.21)	0.16	0.19	(0.22)	(0.25)
λ_{r1}	45.5	9.3	6.0	(4.63)	(3.66)
λ_{r2}	(3.7)	<0.36	<0.36	(<0.36)	(<0.36)
K_{01}	12.0	10.9	10.9		
K_{02}	14.4	13.4	13.4		
K_{03}	12.9	12.0	12.0		
λ_{s1}	1.26	1.40	1.40		
λ_{s2}	0.60	0.57	0.57		
λ_{s3}	0.30	0.25	0.25		
δ_1	0.6_{32}	1.0	1.0		
δ_2	0.8_{37}	1.2_{25}	1.2_{25}		
δ_3	0.6_{32}	1.2_{25}	1.2_{25}		
δ_3	0.6_{32}	1.0	1.0		
σ_1/λ_{r1}	0.385	0.376	0.357	(0.341)	(0.325)
σ_0	17.7	3.67	2.34	1.80	1.44

[a] ( ) indicates tentative estimates.
[b] For units see note under Table I.

led to the results summarized in the first column of Table II. These parameters are used in calculating the solid curves shown in Fig. 6.

Tungsten at room temperature differs from nickel in that there is no clear evidence of more than one free-electron term on the basis of optical data alone. In fact the data may be fitted very well with a single such term in addition to the three bound-electron terms already mentioned. In this case the conductivity associated with the single term will be just half of the observed dc conductivity. The difficulty in satisfying Eq. (7) is removed by adding a second free-electron term. Without more complete data one can only guess tentative values for σ_2 and λ_{r2}, which are shown in parentheses in Table II. Perhaps this interpretation will have to be revised when data on optical constants at longer wavelengths or data on electronic mean free path become available. Note that the uncertainty about σ_2 does not exist at the higher temperatures.

The experimental results for tungsten at 1100°K and 1600°K are shown in Figs. 7 and 8. In making these measurements a substantial amount of radiation was produced by the tungsten ribbon itself. This radiation did not pass through the light chopper, however, and thus produced no modulation of the current in the photocell. No output reading was obtained when the primary light source was turned off. The intensity of the radiation produced by the tungsten sample was checked independently by relocating the light chopper. In this way it was ascertained that the steady radiation from the sample would not overload the photocell or modify its sensitivity to the chopped primary radiation.

A common set of bound-electron terms proved entirely adequate in the analysis of data at both 1100°K and 1600°K. These terms are not quite the same, however, as those adopted for room temperature. The parameters are listed in the appropriate columns of Table II. Two free-electron terms were indicated in the high temperature data. However, the second free-electron term seemed to have a very short characteristic wavelength in comparison with that postulated at room temperature. The curves in Figs. 7 and 8 were calculated using the parameters given in Table II.

The data at the higher temperatures seem to fall in a regular pattern, since the bound-electron terms appear relatively constant while σ_2 and σ_1/λ_{r1} vary only a little. Hence it seems fairly safe to extrapolate these parameters to still higher temperatures. The dc conductivity of tungsten shown in Table II is that reported by Forsythe and Watson.[30] From these values one can get a good estimate of σ_1 at higher temperatures. λ_{r1} may then be derived from the assumed ratio σ_1/λ_{r1}. Values of the free-electron parameters estimated in this way for 2000°K and 2400°K are given in the last two columns of Table II. These estimated parameters will be used in the following calculation of spectral emissivity.

VI. THE SPECTRAL EMISSIVITY OF TUNGSTEN

The normal spectral emissivity of a heated plane surface is by definition the ratio of the energy radiated normal to the surface in a narrow range of wavelength to that which would be radiated by an ideal radiator or "blackbody." By Kirchhoff's law this is one minus the reflectivity at normal incidence. If the electromagnetic fields obey Maxwell's equations, then the reflection of light will be governed by the complex dielectric constant K in the manner already discussed. It is more convenient to express the emissivity as a function of the complex index of refraction, $n-ik$, which is simply the square root of K. Then the emissivity, e, is:

$$e=\frac{4n}{(n+1)^2+k^2}. \tag{8}$$

Appropriate values of n and k may be found by taking the square root of K as determined by experiment or as

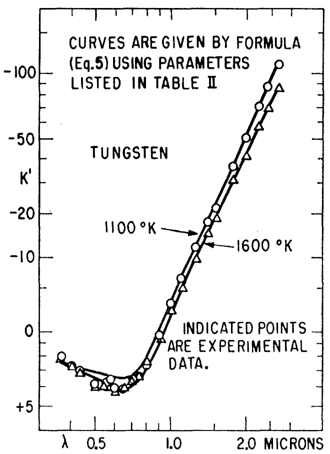

FIG. 7. Real part of dielectric constant of tungsten at 1100°K and 1600°K.

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[30] W. E. Forsythe and E. M. Watson, J. Opt. Soc. Am. 24, 114 (1934).

calculated by Eq. (5). The emissivity of tungsten was calculated in this way using Eq. (5) with the parameters shown in Table II. The results of this calculation are shown in Fig. 9 for the temperatures 1100, 1600, 2000, and 2400°K.

It is of interest to compare the calculated emissivities shown in Fig. 9 with the observations of De Vos.[31] His data are not reproduced here, but are in close quantitative agreement at 0.4 micron and not quite so good agreement with ours at 1.0 micron and longer. The calculated curves intersect at a common point, thereby indicating a cross-over point similar to that observed by De Vos, but at a wavelength 1.13 micron instead of 1.27. Furthermore, the emissivities shown in Fig. 9 are somewhat lower than the values observed by De Vos at the longer wavelengths. Notwithstanding these differences, the similarity of the two sets of curves is very remarkable considering the different sources of information on which they are based and the fact that the present work depends on an extrapolation to obtain data at temperatures above 1600°K, while De Vos depended on an extrapolation to get many of his data below 2000°K.

The fact that emissivity curves in the present work are calculated from analytic expressions for K, makes it possible to find out what features in this analysis are responsible for a crossover of the type demonstrated in Fig. 9. This is a question of general interest because Price,[21] Weale[32] and Marple[33] have observed similar crossover points or x-points in various other metals such as Pt, Pd, Mo, Ta, and Re. Marple[34] has observed an x-point in Nb at 0.7 to 0.75 μ; and similar x-points in the following compounds: ZrN at 0.46 μ, HfN at 0.52 μ, TaC at 0.73 μ, and ZrC at about 2 μ. On the basis of these experiments it appears that the existence of an x-point may be a quite general phenomenon in metallic conductors. Some conflicting evidence appears in the above literature concerning possible x-points in Ni and Cu as well as other metals with optical properties having generally low temperature coefficients. Since the changes in emissivity of these metals are quite small, the question of x-points in them may be largely academic until more precise methods of measuring emissivity are developed.

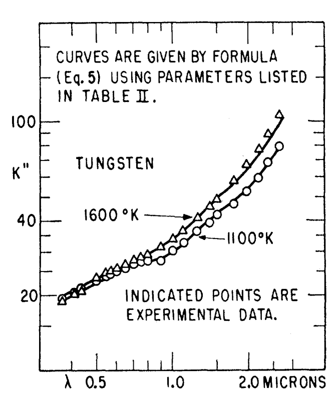

FIG. 8. Imaginary part of dielectric constant of tungsten at 1100°K and 1600°K.

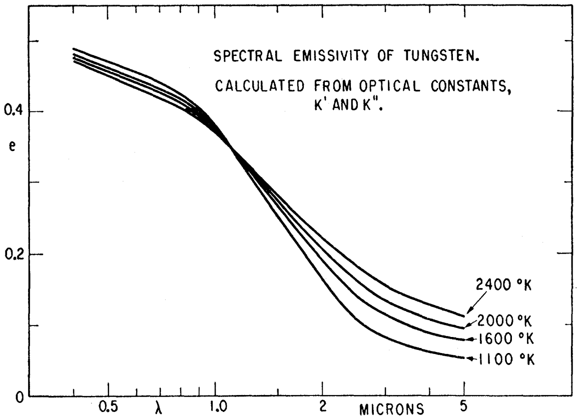

FIG. 9. Calculated spectral emissivity of tungsten.

The theory of Weil[35] appears to be inadequate to explain the existence of x-points, because it indicates that the cross-over wavelength λ_x should be proportional to λ_{r1}, which depends on temperature. Both direct experiment and the calculated curves shown in Fig. 9 indicate that λ_x is independent of temperature. In the present interpretation, the temperature dependence of emissivity at wavelengths greater than λ_x appears to be almost entirely due to the free-electron term containing σ_1 and λ_{r1}. While both of these parameters depend upon temperature, they maintain a nearly constant ratio. If they did not do so, the calculated values would be inconsistent both with observed values of K and with observed emissivity. However, it seems quite definite that only a small part of the observed temperature dependence of emissivity at wavelengths less than λ_x might be attributed to changes in σ_1 and λ_{r1} if their ratio were constant. This follows from the same reasons which explain the smallness of the temperature coefficient in nickel. At wavelengths below λ_x the temperature coefficient of emissivity seems to be largely influenced by the variations in σ_2 in the present analysis. Perhaps just as good an alternative case could be made in which the temperature coefficient in this wavelength range would be attributed to some other cause. It may be premature to try to settle this point at the present time.

VII. DISCUSSION

It seems to be true in general that most of the dc conductivity is contained in σ_1, and this is thought to be the only component of conductivity which depends significantly on temperature. The smallness of the

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[31] J. C. De Vos, Physica **20**, 690 (1954).

[32] R. Weale, Proc. Phys. Soc. (London) **A62**, 661 (1949).

[33] D. T. F. Marple, J. Opt. Soc. Am. **46**, 378 (1956); **46**, 490 (1956).

[34] D. T. F. Marple (private communication).

[35] R. Weil, Proc. Phys. Soc. (London) **60**, 8 (1948).

temperature dependence of K' and K'' in some metals, notwithstanding large changes of conductivity, must then be attributed to the small changes of the term in Eq. (5) which contains σ_1. Since in all the author's measurements of nickel $\lambda \ll \lambda_{r1}$, one may simplify this term in the following way:

$$\sigma_1/(\lambda_{r1}-i\lambda) \cong \sigma_1/\lambda_{r1}+i\sigma_1\lambda/\lambda_{r1}^2. \qquad (9)$$

Now, if λ_{r1} varies with temperature in direct proportion to σ_1, it is evident that the real part of Eq. (9) will remain constant and likewise K' will be independent of the temperature no matter how much σ_1 may change. Likewise, if the imaginary part of Eq. (9) is much smaller than the imaginary part of $\sigma_2/(\lambda_{r2}-i\lambda)$, the changing values of σ_1 and λ_{r1} with temperature may produce only relatively small changes in K''. The smallness of K_{r1}'' is evident, for example, in Fig. 3. The actual differences between the values of K'' of nickel at 88°K and 473°K at 2 microns and above in the curves in Fig. 4 are mostly due to the small but finite differences in the imaginary part of Eq. (9). A similar explanation may be proposed for the vanishingly small temperature coefficient of optical properties of several other metals studied by Drude[1] in a range of temperature spanning substantial changes of conductivity. The foregoing arguments therefore support the deduction that in nickel at least, and perhaps also in some other metals, the ratio σ_1/λ_{r1} is independent of temperature despite large changes in σ_1.

The anomalous skin effect has been proposed as a mechanism giving rise to deviations from Maxwell's equations. Undoubtedly such deviations do exist and may be observed in any metal in an appropriate range of wavelength and temperature, i.e., microwaves at very low temperatures. Possibly there are some metals in which such deviations might be observed at infrared wavelengths and at room temperature. However, in regard to optical properties at ordinary temperatures in metals having two classes of free electrons, the effect may not be important at all. The reason for this is based on the same logic that explains the very low temperature coefficient of K' and K'' for nickel and certain other metals. The mean free path of the class of electrons which contributes most to the conductivity in these metals may have a sizable temperature coefficient. But, when this mean free path is reduced by increasing the temperature, there is almost no change in the ratio σ_1/λ_{r1} or in the optical properties, as has already been noted. Since these properties are independent of the mean free path it may be expected that they would also be independent of anomalies in the mean free path near the surface. As a corollary no difference between surface optical properties and bulk properties is to be expected in such metals.

There is nothing in the foregoing analysis which refutes the excellent work on electronic mean free path in metals by Sondheimer[22] and others. However, in applying the mean free path concept to optical properties, it must be recognized that the mean free path of those electrons which contribute most to the dc conductivity may not have much influence on optical properties. It is evident that there is a great need for more experimental data both in regard to optical properties and mean free path effects in order to clarify the interrelation between these two phenomena.

Several authors observed a superficial agreement of optical properties of certain metals with the simplified theory based on one type of free electron. But this treatment led to too low values for the conductivity. The alternative explanation leading to the correct conductivity is given in paper I. It was also recognized long ago that optical properties of another group of metals did not agree even superficially with the simplified theory. Nickel appears to be such a metal according to measurements in the visible and near infrared wavelength range. In the author's interpretation this behavior results from the fact that the second class of free electrons has its region of dispersion centered in just this range. Beattie and Conn,[15,36] by making measurements on nickel at much longer wavelengths, succeeded in establishing a superficial agreement with simple theory in that range, as might be expected. In their interpretation, the failure of simple theory at the shorter wavelengths was attributed to "resonance absorption," i.e., bound-electron terms. Evidently they did not consider it important to back up this interpretation with any sort of quantitative test.

Beattie and Conn in their simplified treatment did not find agreement either with the observed dc conductivity or with its temperature coefficient. The author's treatment is in quantitative agreement with both. The analysis given here has the further virtue that, while it was based on measurements only up to 2.65 μ, it is sufficiently accurate for extrapolation to much longer wavelengths, where it agrees rather well with the experiments of Beattie and Conn.

It is not inherent in Drude's analysis that the number of classes of free electrons should be limited to two, so that in principle there may be more than two such classes or there may be only one. In this connection it is interesting to note that Kent[37] and Schulz[16] between them reported that the liquid metals Bi, Pb, Cd, Sn, Hg, and Ga all obey the simplified formulas derived under the assumption of a single class of free electrons and have a dc conductivity in agreement with that derived from optical data. There seems to be no question of any surface anomaly in these metals or of any deviation from Maxwell's equations.

The principal conclusions of this paper have to do with the free-electron terms. However, the analysis summarized in Tables I and II also indicates some regularities in the bound-electron terms. It seems that λ_{sm} does not change much with temperature, while δ_m

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[36] J. R. Beattie and G. K. T. Conn, Phil. Mag. 46, 1002 (1955).

[37] C. V. Kent, Phys. Rev. 14, 459 (1919).

is generally greater at higher temperatures. In nickel K_{01} seems to increase in proportion to δ_1, but a similar trend is not followed in tungsten. For the present, no explanation will be attempted for these observations concerning bound-electron terms, and they should be regarded as tentative.

The very large contribution of bound electrons to the optical properties of tungsten might tend to indicate an unusually high electronic polarizability of the tungsten atom or ion. Note that $(1+\sum_m K_{0m})$ is of the order of 40 for tungsten as compared to about one-tenth this value for nickel. The indicated high polarizability of tungsten might explain the anomalous dielectric properties of certain of its compounds, as for example, WO_3.

VIII. CONCLUSIONS

Experimental data for optical constants of nickel and tungsten at different temperatures are interpreted according to a formula for complex dielectric constant given by Drude. If the various terms in this formula may be attributed to different classes of free and bound electrons, then it may be said that the formula allows for the existence of more than one class of free electrons. Each class of free electrons accounts for a portion of the dc conductivity and has its own characteristic relaxation wavelength, which appears as a parameter in the formula. Drude's formula as interpreted here does not constitute a theory in itself, but the results of an analysis of experimental data based on this formula are conceived to be a likely effective source of quantitative information which it is hoped will be coordinated with nonoptical data in formulating a more specific and more complete atomic theory.

Agreement is reached in all cases between the observed optical properties and the dc conductivity. The interpretation of the results for nickel is tested by extrapolation to longer wavelengths where calculated optical constants and their temperature coefficients are in reasonably good agreement with the experiments of Beattie and Conn. The data for tungsten are tested by calculating spectral emissivities at different temperatures from them. These results compare well with the measurements of De Vos.

The analysis of experimental data in this manner gives the interesting result that most of the dc conductivity may be attributed to one class of free electrons, although in some metals a second class and in nickel even a third class are needed in addition to the bound electrons in order to account for the observed optical properties. In both nickel and tungsten the characteristic wavelength λ_{r1} of the first class of free electrons proves to be proportional to the corresponding conductivity σ_1 at different temperatures. In nickel the constant ratio σ_1/λ_{r1} accounts for the low temperature coefficient of optical properties throughout the visible and near infrared wavelength range. The optical properties of tungsten change more rapidly with temperature, but the constant ratio of σ_1/λ_{r1} contributes to the vanishing temperature coefficient of the emissivity at a single wavelength. The constancy of this ratio is also supported by a theory in which the concentration and effective mass of the appropriate class of free electrons are thought to be independent of temperature.

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